THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

Levels of Polycyclic Aromatic Hydrocarbons in Water from Nairobi River, Nairobi County-Kenya

Nawiri M.P.
Senior Lecturer, Department of Chemistry, Kenyatta University, Kenya
Nyambaka H.N.
Professor, Department of Chemistry, Kenyatta University, Kenya
Mobegi E.
Ph.D. Student, Department of Chemistry, Kenyatta University, Kenya

Abstract:
Nairobi city is the economic and industrial hub for Kenya with increasing industrialization and urbanization. River Nairobi is one of the major rivers in the Nairobi river basin. The river has become a repository for industrial and domestic waste. This has necessitated and environmental issue and more so on its unknown levels of hazardous persistent organic pollutants in particular the polycyclic aromatic hydrocarbons (PAH). Notably, its untreated water from some sections along its course way is used for domestic purposes hence poseshuman health risks that may be attributed to long term exposure and accumulation of PAH. This study analyzed the concentration of 16 US EPA PAHs and compared the levels with US EPA and WHO standards in order assess the potential risks that people using water from this river might be exposed to.The sampling points were chosen based on the various activities such as informal and formal settlements, industrial area andmicro-enterprises 'Jua kali' activities. PAHs from water samples were extracted, cleaned prior to identification and quantified by GC-MS. The total concentrations of 16 PAHs ranged between 5.19 ng/L and 9.14 ng/L with an overall mean of 10.08 ng/L. Generally, the results show that water from the river was contaminated with PAHs although the levels were below the recommended WHO limit of 50 ng/L. However, it is feared that continuous use of their water by man may result to risk exposure to PAHs. Therefore precaution needs to be taken in the use of untreated water from Nairobi River in fear of body accumulation of PAHs and their dangers.

Keywords: *physico-chemical parameters, Polycyclic Aromatic Hydrocarbons, Nairobi River*

1. Introduction

Environmental degradation has become a major concern globally. The harmful substances in our environment, which are introduced by man either intentionally or accidentally, have been found to have adverse effects on human life, agriculture and the aquatic life.Water pollution has been ranked the second most important environmental issue next to air pollution (1). Nairobi River flows through the heart of Nairobi City which is one of the industrial cities in Kenya. The city, in the recent past, has experienced exponential growth in industrialization and population. However, this growth has not been matched by development of infrastructure such as sewer systems and solid waste management facilities. Consequently, this has led to pollution of the water resources with pollutants such as polycyclic aromatic hydrocarbons (2; 3).

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic chemicals consisting of two or more aromatic rings. Sixteen (16) PAHs are considered as priority by the European Union environmental protection agency, ATSDR, USEPA and WHO. These include naphthalene acenaphthylene acenaphthene fluorene phenanthrene anthracene fluoranthene benzo(a)anthracene chrysene benzo(b)fluoranthene benzo(k)fluoranthene benzo(a)pyrene, indeno(1,2,3-cd)pyrene dibenz(ghi)anthracene benzo(ghi)perylene and pyrene (4)The existence of PAHs in the environment is increasingly becoming a concern due to their adverse effects on human health and toxicity to aquatic life as a result of their carcinogenicity and mutagenicity (5; 6; 7). In the biennial ranking comprised of chemicals deemed to pose the greatest danger to human health, PAHs were ranked tenth in 1999, fifth in 2001 and seventh in 2005 (8). In terms of toxicity, PAHs can be classified into low-molecular weight PAHs (LMPAHs) possessing two or three carbon rings and high-molecular weight PAHs (HMPAHs) possessing four or more carbon rings. PAH solubility decreases with increasing molecular weight. Bioaccumulation of PAHs by organisms is generally greater for the lower molecular weight and more water-soluble compounds than for the higher molecular weight compounds. The LPAHs have been shown to be acutely and chronically toxic and can impair survival and growth by causing abnormal reproduction and development (9).

Data from Nairobi cancer registry indicate that cancer cases are on the rise. This is attributed to a number of factors ranging from nutrition, physical life style to fears of exposure to possible sources of carcinogenic compounds such as PAHs (10; 11).It is an unfortunate scenario that water from Nairobi River is used for domestic and agricultural purposes though feared to be polluted. Therefore the people could be exposing themselves to these PAHs which are known to be carcinogens by consuming food grown using the contaminated water especially vegetables. Potential sources of PAHs in environment surrounding Nairobi city include discharge of untreated industrial waste from light industries in Kariobangi, domestic sewage from informal settlements (slums) such as Kibera and Mkuru kwa Reuben, poor disposal of used crankcase oil and grease from vehicle repair garages like the Ngara area and Gregory. Other sources include petrol spills, vehicular emissions, leaching of waste from the Dandora public dumping site and asphalt and tar from road construction.

In Kenya, very little information is available on the distribution and levels of PAHs in the environment. Thus, the primary focus of this study is to determine the levels of PAHs in surface water from Nairobi river which will provide base line information with regard to PAHs contamination. This further will inform policy institutions such as National Management Environmental Authority (NEMA) to prioritize PAHs under the Environment Management and Coordination Act (EMCA). This is to ensure that any exceedance in concentration over environmental quality standards can be detected and appropriate actions can be taken.

2. Materials and Methods

2.1. Chemicals and Reagents

All chemicals and reagents were of analytical grade. Dichloromethane (DCM) hexane, high purity nitrogen, anhydrous sodium sulphate, florisil, phosphate buffer (pH 6.8), Silica gel and aluminium oxide, were obtained from Sigma Aldrich, UK. A PAH standard mix containing the 16 priority PAHs was obtained from Dr. Ehrenstofer Augsburg, Germany.

2.2. Instruments and Instrumental Conditions

An Agilent 7890A Gas Chromatography and 5975C Mass Selective Detector was used for the analysis. Column oven temperature was programmed from 35 to 280 ^{o}C with initial temperature maintained for 5 min then 10^{o}C/min to 280^{o}C for 10.5 min and then for 29.9 min at 50 ^{o}C/min to 285 ^{o}C. The GC was fitted with a HP-5 MS low bleed capillary Column (30m x 0.25 mm i.d., 0.25µm film thickness). The carrier gas was helium.

2.3. Sampling

Surface water samples were collected directly into clean sterilized 500mL sample bottles. Three replicate samples were collected at the same sampling station. The sample bottles were amber colored to prevent UV light from effecting degradation of the target compounds. All samples were stored in an icebox at 4^{o}C and transported to laboratory for extraction and analyses. In the laboratory samples were stored at temperatures of 4 ^{o}C.

2.4. Extraction and Clean-Up

Extraction was carried out by liquid-liquid extraction following a modified procedure outlined by Anyakora and Herbert, (12). Duplicate water samples were mixed with phosphate buffer to stop any micro-organic process. The samples were passed through glass wool to remove sediments and coagulations. 100 mL of the sample was measured with a volumetric flask and extracted with 20 mL of DCM in a separatory funnel. The mixture was shaken for 2 minutes and allowed to separate for 5 minutes. The bottom layer was decanted into a pre-cleaned and labeled flask and wrapped in foil.

For clean up, the extract was passed through slurry packed with silicagel, aluminum oxide and anhydrous sodium sulfate in that order. The column was washed with 15 ml of hexane and the eluant was collected by eluting the column with 100 mL of hexane and 100 mL of dichloromethane. The eluate was then concentrated to about 3 ml using a rotary evaporator which was further reduced to about 0.5 mL using a stream of gaseous nitrogen.

2.5. Identification and Quantification of PAHs

Identity of PAHs in the samples was confirmed by the retention time and abundance of quantification/confirmation ions and mass spectra match against the calibration standards using PAHs standards. Calibration standard of 0.1ng/L, 0.5 ng/L 1 ng/L, 5 ng/L and 10 ng/L were prepared. Confirmation of identity of the analytes was done using NIST/EPA/NIH MASS SPECTRAL LIBRARY (NIST 05) and NIST MASS SPECTRAL SEARCH PROGRAM Version 2.0d. Quantification was performed using the calibration curves. The efficiency of recovery procedure was assessed using percent recoveries of the PAHs. This involved spiking of the water samples with known concentrations of the standard solution. The recovery test water samples were subjected through the same extraction, clean-up and instrumentation procedures as for the water samples to be analyzed.

3. Results and Discussion

Average recovery percentages of the spiked samples in the GC-MS ranged from 61.23 to 72.89 % for the standards (Table 1)

Peak no.	Compound	RSD (%)	Recovery (%)
1	Naphthalene(NA)	8.2	72.89
2	Acenaphthylene (ACL)	5.7	70.64
3	Acenaphthene (AC)	4.4	64.73
4	Fluorene (FL)	1.2	71.12
5	Phenanthrene (PHE)	9.5	61.62
6	Anthracene (AN)	8.6	71.25
7	Fluoranthene (FA)	4.8	72.64
8	Pyrene (PY)	5.9	64.94
9	Benz (a) anthracene (BaA)	9.6	71.34
10	Chrysene (CHR)	8.7	62.61
11	Benzo(b) fluoranthene (BbFA)	7.6	70.64
12	Benzo(k) fluoranthene(BkFA)	9.1	63.28
13	Benzo(a)Pyrene (BaP)	4.2	61.84
14	Indeno(1,2,3-cd) Pyrene(IP)	9.5	61.23
15	Dibenzo(ah)anthracene(DBahA)	8.7	64.78
16	Benzo(ghi)perylene (BghiP)	8.2	64.32

Table 1

The low percent recoveries could be attributed to high a flow rate such that the compounds did not have sufficient time and contact to adsorb to the surface or the surface of the solid surface did not sufficiently match the polarity of the PAHs. The method used had average relative standard deviation ranging from 1.2 to 9.6% implying that the individual measurements were close to the mean value and hence high precision of the results

3.1. PAHs in Water

Results on the levels and distribution of PAHs in Nairobi River are summarized in table 2

PAHs	No.of Rings	Race-course	Outering	Dandora	P-value	Overall Mean
Naphthalene	2	0.14 ± 0.01^{c}	0.16 ± 0.00^{b}	1.17 ± 0.00^{a}	<0.001	0.49±0.00
Acenaphthylene	3	ND	ND	ND	ND	ND
Acenaphthene	3	ND	ND	ND	ND	ND
Fluorene	3	ND	1.14±0.00	0.67±0.00	<0.001	0.91±0.07
Phenanthrene	3	ND	2.17±0.00	0.66±0.00	<0.001	1.42±0.22
Anthracene	3	ND	0.55±0.00	1.18±0.00	<0.001	0.87±0.09
Fluoranthene	4	ND	0.98±0.00	0.22±0.00	<0.001	0.60±0.11
Pyrene	4	ND	1.67±0.01	0.18±0.00	<0.001	0.92±0.22
Benzo(a)anthracene	4	1.68 ± 0.01^{c}	0.28 ± 0.00^{b}	0.07 ± 0.00^{a}	<0.001	0.68±0.17
Chrysene	4	3.57 ± 0.09^{c}	0.47 ± 0.00^{b}	0.06 ± 0.00^{a}	<0.001	1.37±0.38
Benzo(b)fluoranthene	5	0.08±0.00	0.09±0.00	0.08±0.00	<0.001	0.08±0.00
Benzo(k)fluoranthene	5	3.67±0.22	ND	0.18±0.00	<0.001	1.92±0.54
Benzo(a)pyrene	5	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	5	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	6	ND	ND	ND	ND	ND
Benzo(ghi)perylene	6	ND	ND	ND	ND	ND
∑ PAH measured		9.14	7.51	5.19		10.08

Table 2: Mean±SEConcentrations (ng/L) and Distribution of PAHs in the Nairobi River

Mean values followed by the same small letter within the same row are not significantly different (One-way ANOVA, Duncan's test, α=0.05)

The total PAHs concentrations in the Nairobi River water were within the range of values reported for water from various sites along polluted rivers in the world. For example, Maldonado *et al.* (13) in Aegean Sea reported PAHs concentration ranging from 0.113 – 0.489 ng/L with a mean of 0.216 ng/L. A similar concentration range of 4 – 36 ng/L with a mean concentration of 20 ng/L was reported for Seine River and Estuary in France (14). However, higher PAHs concentrations compared to those that were found in Nairobi River have been reported. For instance, in Chesapeake Bay, USA total PAHs ranged between 20 and 65.7 ng/L with an average of 33.3 ng/L (15). In water bodies around England and Wales, the total concentration of PAHs was found between <1 and 24,821 ng/L (16).

Much higher PAHs concentration have been reported in Northern Greece and China ranging from 184 ng/L to 856 ng/L and 106 to 26920 ng/L, respectively (17; 18; 19; 20). The levels of PAHs along the Nairobi River had a general decrease of the levels of PAHs attributed to the dilution effect. Race-Course sampling site had the highest total PAHs concentration of 9.14 ng/L amongst all the sampling stations followed by Outering and Dandora with concentrations of 7.51 ng/L and 5.19 ng/L respectively. This sampling site is situated near Gregory and Ngara car garages and Ngara market associated with poor disposal of crankcase oil and grease from the car garages and accumulated agricultural waste from the Ngara Market respectively (21). Additionally, there are so many vehicles travelling constantly in the area which could also be a potential atmospheric sources of PAHs detected (18; 19).

The detected PAHs varied from one sampling station to another. It is important to note there is no single sampling station where all the 16 PAHs were detected. Majority of 3-ring and 4-ring PAHs were not detected at Race-course but were detected at Outering sampling stations (table 2). This is can be attributed to either these PAHs being non-existent or present in a concentration lower than the detectable limit.The absence of 5 –ring PAHs such as benzo(a)pyrene and indeno(1,2,3-cd)pyrene and 6-ring PAHs such as dibenz(a,h)anthracene and benzo(ghi)perylene can be related to their tendency to be adsorbed to sediments and soil, low water-solubility and being more lipophilic (22;9).

The PAHs distribution in Nairobi River showed that only chrysene, benzo(b)fluoranthene and benzo(a)anthracene were detected in all the sampling sites Table 2. The PAHs distribution at Race-course was observed with benzo(k)flouranthene recording the highest mean concentration of 3.67 ± 0.22 ng/L and benzo(b)fluoranthene with the least concentration of 0.08 ± 0.00 ng/L. The PAHs distribution at Outer Ring Road showed that Phenanthrene recorded the highest concentration of 2.17 ± 0.00 ng/L and benzo(b)fluoranthene with the least concentration level of 0.09 ± 0.00 ng/L. Finally, at Dandora sampling site, anthracene recorded the highest concentration of 1.18 ± 0.00 ng/L whereas chrysene recorded the least concentration of 0.06 ± 0.00 ng/L. It is gratifying to note that most of the PAHs were detected at this sampling station. This observation could be attributed to the fact that the Dandora dumping site could be associated with chemical leachetes which might have PAHs among other chemical pollutants. With increasingly intense urban and industrial development around Nairobi River, the amount of PAHs detected is likely to be related to urban runoff, sewage outfalls and wastewater discharges, which were observed during sampling.

The 16 PAHs were divided into three groups as mentioned earlier.The 2- & 3-ring PAHs were predominant in water from Nairobi River with mean of 37%; the percentage composition for the 4-ring was 35% and 28% for 5- and 6-ring PAHs. The percentage of 2 -& 3 and 4 ring PAHs can be linked to combustion products from low temperature pyrolytic processes and/or petrogenic sources (19; 23; 24). The high percentage of low and medium molecular weight PAHs confirms the source of PAHs to be from combustion products from low temperature pyrolytic processes and/or petrogenic sources such as oil leakages or inadvertent oil spills (24).

From Table 2 there were significant differences in the mean concentration of the detected PAHs. Higher concentrations of Benzo(a)Anthracene, chrysene and benzo(k)fluoranthene were observed at Race-course sampling site. The higher levels of these PAHs compared to others could be attributed to used crank case oil, grease and other related waste from garages in the larger Ngara area. Anthracene showed significant difference ($p<0.05$) in all the sampling sites with Dandora recording highest mean concentration of 1.18 ± 0.00 ng/L and Outer Ring Road recording the lowest concentration of 0.55 ± 0.00 ng/L. Benzo(a)anthacerene showed a siginificant difference ($p<0.05$) in all the sampling sites with Race-course recording maximum mean value of 1.68 ± 0.0ng/L and Dandora recording a minimum concentration of 0.07 ± 0.00 ng/L.

The presence of priority PAHs in the Nairobi River may be attributed to various sources. First, the Nairobi River navigates through the Nairobi central business district where it receives heavy smoke from vehicles that move constantly on the roads. Secondly, it is also suspected that effluent from broken sewer lines, as observed during sampling period, get into the river which may also contribute to the level of pollution. Thirdly, the river also receives a lot of industrial waste from light industries from Kariobangi area as a result of transportation by the Mathare River when it joins the Nairobi River. Finally, the waste disposal site at Dandora which is the largest in Nairobi County (study area) contributes to leaching of waste into this river when it rains and during the burning process which is the main process of disposing waste at this dumping site.

4. Conclusion

The results from the Ngong and Nairobi rivers indicated that the study area was contaminated with a wide range of PAHs. The type of PAHs detected varied from one location to another. The commonly found PAHs compounds in the water samples from both Ngong and Nairobi rivers were fluorene, phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, naphthalene, dibenz(a,h)anthracene, dibenz(a,h)anthracene and chrysene.The predominance of low and medium molecular weight PAHs (PAHs with 2-3 rings) in water from both rivers reflects petrogenic origin, related to petroleum including crude oil and its refined products.

5. References

i. WHO 1997. Water Pollution Control - A Guide to the Use of Water Quality Management Principles. Great Britain: WHO/UNEP.
ii. Okoth, F., and Otieno, P. (2001), Pollution Assessment Report of the Nairobi River Basin, UNEP. AWN, Nairobi, pp. 106.
iii. Budambula, N., and Mwachiro E. (2006). Metal status of Nairobi river waters and the bioaccumulation in Labeo Cylindricus. Water, Air, and Soil Pollution, 169: 275–291.
iv. Martinez, E., Gros, M., Lacorte, S., & Barcel, D. (2004). Simplified procedures for the analysis of Polycyclic aromatic hydrocarbons in water, sediments and mussels. Journal of Chromatography, 1047: 181-188.
v. Metre,V., Barbara M., Scoggins, M., & HamiltonP. (2006). Parking Lot sealcoat: A Major Source of Polycyclic Aromatic Hydrocarbons (PAHs) in Urban and Suburban Environments.

vi. Kanchanamayoon, W., & Tatrahun, N. (2008). Determination of polycyclic aromatic hydrocarbons in water samples by solid phase extraction and Gas Chromatography. World Journal of Chemistry, 3: 51-54.

vii. Wang, J,Kai, Z.,Bo, L.,& Eddy Y. (2011). Occurrence, source apportionment and toxicity assessment of polycyclic aromatic hydrocarbons in surface sediments of Chaohu,Journal of EnvironmentalMonitoring,13:3336.

viii. King S., Meyer J. S., Andrews A. R. J. (2002). Screening Method for Polycyclic Aromatic Hydrocarbons in Soil Using Hollow Fibre Membrane Solvent Microextraction. Journal of Chromatography, 201-208.

ix. Ololade, I. A. and Lajide, L. (2010). Exposure level and bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in edible marine organisms. Journal of Environmental Indicators, 5: 69-88.

x. Teaf, M. (2008). Polycyclic aromatic hydrocarbons in urban soil: A Florida risk assessment perspective. International Journal of Soil, Sediment and Water, 1: 2.

xi. Zhang, W., Chaohai, W., Chunhua, F., Zhe, Y., Man R., Bo, Y., Pingan, P., & Jiamo, F. (2011). Distribution and health-risk of polycyclic aromatic hydrocarbons in soils at a coking plant. Journal of Environmental Monitoring,13:3426-3436

xii. Anyakora, C.& Herbert, C. (2006). Determination of polynuclear aromatic hydrocarbons (PAHs) in selected water bodies in the Niger Delta. African Journal of Biotechnology, 21: 2024-2031.

xiii. Maldonado, C., Bayona, M., & Bodineau, L. (1999). Sources, distribution and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. Environmental Science and Technology 33: 2693-2702.

xiv. Fernandes, B., Sicre, M., Boireau, A., & Tronszynski, J. (1997). Polyaromatic hydrocarbon distributions in the Seine River and its estuary. Marine Pollution Bulletin, 34: 857-867.

xv. Gustafson, E., & Dickhut, M. (1997. Distribution of polycyclic aromatic hydrocarbons in Southern Chesapeake Bay surface water: evaluation of three methods for determining freely dissolved water concentrations. Environmental Toxicology and Chemistry, 16: 452-461.

xvi. Law, R., Dawes, V.J., Woodhead, R., & Matthiessen, P. (1997). Polycyclic aromatic hydrocarbons in seawater around England and Wales. Marine Pollution Bulletin, 34: 306-322.

xvii. Manoli, E., Samara, C., Konstantinou, I., & Albanis, T. (2000). Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. Chemosphere, 41: 1845-1855.

xviii. Zhou L., and Maskaoui K. (2003). Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. Environmental Pollution, 121: 269–281.

xix. Maskaouia, K., Zhoub L., Honga, H., & Zhanga Z. (2002). Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China. Environmental Pollution, 118: 109–122.

xx. Zhang, Z., Jun, H., Gang, Y., & Huasheng, H. (2004). Occurrence of PAHs, PCBs and Organochlorine pesticides in the Tonghui River of Beijing, China. Environmental Pollution, 130: 249-261.

xxi. Essumang, D., Adokoh, C., Afriyie, J., & Mensah, E. (2009). Source assessment and analysis of polycyclic aromatic hydrocarbon in the Oblogo waste disposal sites and some water bodies in and around the Accra metropolis of Ghana. Journal of Water Resource and Protection, 1: 456-468.

xxii. Sarrazin, Luc, Diana, Catherine, Wafo, Emmanuel, Pichard-Lagadec, Véronique, Schembri, Thérèse Monod, & Jean-Louis. (2006). determination of polycyclic aromatic hydrocarbons in marine, Brackish, and River Sediments. Journal of Liquid Chromatography & Related Technologies, 29: 69 - 85.

xxiii. Stein, D., Tiefenthaler, L., & Schiff, K. (2005). Watershed-based sources of polycyclic aromatic hydrocarbons in urban storm water. Environmental Toxicology and Chemistry, 25: 373–385.

xxiv. Okoro, D. (2007). Source determination of polynuclear aromatic hydrocarbons in water and sediment of a creek in the Niger Delta region. African Journal of Biotechnology, 7: 282-285.